Infrared absorption cross-sections, radiative efficiency and global warming potential of HFC-43-10mee

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ABSTRACT

HFC-43-10mee ($C_5H_2F_{10}$) is a substitute for CFC-113, HCFC-141b and methyl chloroform, as well as an alternative to perfluorocarbons with high radiative efficiencies. Recent observations have shown that the global mean tropospheric abundance of HFC-43-10mee has increased steadily from the 1990s to reach 0.211 ppt in 2012. To date, the emission of this compound is not regulated.

The radiative efficiency (RE) of HFC-43-10mee has recently been re-evaluated at 0.42 W m^{-2} ppb^{-1}, giving a 100-year time horizon global warming potential (GWP$_{100}$) of 1650. However, the initial RE, from which the new values were derived, originated from an unpublished source.

We calculated a new RE of 0.36 W m^{-2} ppb^{-1} and a GWP$_{100}$ of 1410 from laboratory absorption cross-section spectra of a pure vapour of HFC-43-10mee. Acquisitions were performed in the 550–3500 cm^{-1} spectral range using Fourier transform spectroscopy. The results were compared with the broadened spectra from the Pacific Northwest National Laboratory (PNNL) database and with theoretical calculations using density functional theory.

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1. Introduction

HFC-43-10mee (also known as 1,1,1,2,2,3,4,5,5,5-Decafluoropentane and 2H,3H-Perfluoropentane, $C_5H_2F_{10}$) is used as a cleaning solvent in electronics and has been investigated as an alternative nonflammable solvent for the recovery of uranium and plutonium [1]. Its estimated atmospheric lifetime is 16.1 years [2]. *In-situ* atmospheric measurements of HFC-43-10me have shown that the global mean tropospheric abundance reached 0.211 ± 0.046 ppt in 2012 [3].

The Fifth Assessment Report (AR5) of the United Nations Intergovernmental Panel on Climate Change [4] used a radiative efficiency (RE) of 0.42 W m^{-2} ppb^{-1} that is based on an unpublished source. To verify this value, we acquired infrared cross-section spectra of a pure vapour of HFC-43-10mee at three temperatures. Composite absorption cross-section spectra have been derived from the data and used to extract the radiative efficiency and global warming potential of the molecule.

2. Experimental setup

Data acquisitions were performed using a Bomem DA8 Fourier transform spectrometer equipped with a Globar source, a KBr beam-splitter and a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. The temperature was measured by a thermocouple directly inserted inside a 10-cm ± 0.1-cm long gas cell. A MKS Baratron gauge was used to monitor the pressure. The pure vapour spectra were recorded in the 550–3500 cm^{-1} spectral range at a resolution of 0.1 cm^{-1} and temperatures of 305.0 ± 0.5 K, 320.0 ± 0.5 K and 340.0 ± 0.5 K. More details on the experimental setup are available elsewhere [5,6].

The HFC-43-10mee sample from Synquest Laboratories had a stated purity of 99%. HFC-43-10mee being liquid at room temperature, several freeze-pump-thaw cycles were performed before allowing the vapour into the cell.

At a given temperature, spectra (each comprising 200 co-added scans with boxcar apodization) are taken at pressures varying from 0.1 to 6 Torr. The effective cross-section for each wavenumber was obtained from a fit of the optical depth versus the pressure using the method described by Sharpe et al. [7]. The optical depths corresponding to very optically thin and optically thick environments were eliminated to obtain a good signal-to-noise ratio while elim-

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inating non-linear saturation effects. The results are pure vapour composite cross-section spectra at the zero-Torr limit.

3. Results and data validation

3.1. Analysis

A survey spectrum of HFC-43-10mee is presented in Fig. 1. Like other fluorocarbons, HFC-43-10mee features a strong absorption band between 1000 and 1500 cm^{-1} due to its C-F bonds. Two other bands of moderate intensities can be seen between 600 and 800 cm^{-1}. Another very weak band associated with the C-H symmetric and asymmetric stretching vibrations lies around 2980 cm^{-1}.

The statistical errors on the composite spectra are taken at the 95% confidence interval (twice the standard deviation). The systematic error (sample purity, pathlength, temperature variation, etc.) is evaluated at 1.4%. This results in uncertainties of 3.5%, 5.6% and 4.3% for the total integrated band strength at 305 K, 320 K and 340 K respectively.

Although the spectral line shape of a compound is usually temperature dependent, the integrated band strengths should remain constant. The experimental cross-section spectra were divided in six spectral bands and the integrated band strength was calculated for each band. The results are presented in Table 1. No significant variation of the values over the studied temperature range were observed.

To estimate the line shape below our detector limit, the wavenumbers and integrated band strengths of the molecule were calculated using density functional theory (DFT) with the B3LYP/6-311+G(2d,p) basis set. From the calculations, a synthetic absorption cross-section spectrum was simulated in the 0–550 cm^{-1} range (see Fig. 1). The synthetic spectrum shows that only weak bands are present in this spectral range. However, as the radiative forcing below 500 cm^{-1} is significant, the synthetic line shapes were included in the calculation of the radiative efficiency of the molecule.

3.2. Isomeric distribution

HFC-43-10mee exists as two diastereomers – *threo* and *erythro* – mixed in solution (see Fig. 2). Each isomer producing its own spectral signature, it was essential to verify that the manufactured sample was representative of the isomeric distribution of HFC-43-10mee in the atmosphere.

Synquest Laboratories provided an approximate ratio of 0.14:0.86 from gas chromatography peaks but could not determine which isomer was dominant. Arnold et al. [3], who also used a sample from Synquest Laboratories, obtained a ratio of 0.17:0.83 using a gas chromatograph-mass spectrometer. Chen et al. [8] worked with a sample of 99% purity from DuPont-Mitsui Fluorochemicals Company and found a 0.12:0.88 ratio using ^{1}H nuclear magnetic resonance spectroscopy and gas chromatography.

Chen et al. [8] also calculated the gas phase reaction of both isomers with OH radicals and concluded that the tropospheric lifetime of *threo-* and *erythro-*HFC-43-10mee were similar. It is therefore expected that the atmospheric isomeric distribution of HFC-43-10mee should remain constant. This result was verified by Arnold et al. [3] who obtained a ratio of 0.16:0.84 from an atmospheric air sample, which was consistent with their manufactured sample. Therefore, it was confidently inferred that the gas sample in this study was representative of HFC-43-10mee atmospheric composition.

However, to get a good estimate of the molecular bands through DFT calculations, it was also essential to know which diastereomer is the most abundant. Arnold et al. [3] used the Chen et al. [8] assumption that *threo-*HFC-43-10mee was dominant. However, no evidence was found in the literature. Therefore, we determined the isomeric composition of the sample by comparing the computed integrated intensities of the fundamental bands of the two diastereomers with our experimental data. *Threo-* and *erythro-*HFC-43-10mee fundamental bands strongly overlap and share comparable intensities. However, the band in the 910–965 cm^{-1} spectral range is isolated enough to be attributed without ambiguity to the calculated single vibration mode v_{18} of *erythro-*HFC-43-10mee (see Fig. 1). This assigns *erythro-*HFC-43-10mee as the dominant isomer. Thus, the synthetic spectrum from 0 to 550 cm^{-1} was created using a mixture of 86% *erythro-*HFC-43-10mee and 14% *threo-*HFC-43-10mee.

3.3. Comparison between experimental and theoretical data

The Pacific Northwest National Laboratory (PNNL) database [7] contains three N$_2$-broadened cross-section spectra of HFC-43-10mee at 278 K, 298 K and 323 K in the 500–6500 cm^{-1} spectral range at an instrumental resolution of 0.112 cm^{-1}. The error is esti-
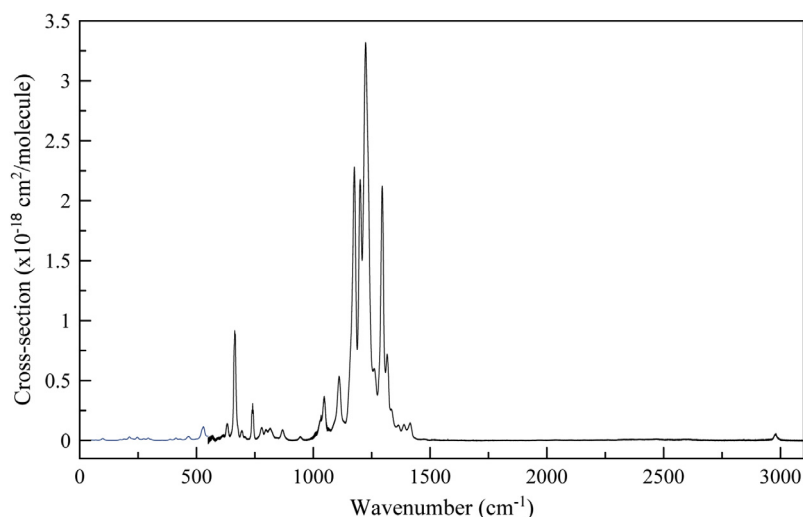

Fig. 1. Composite absorption cross-section spectrum of HFC-43-10mee at 305 K in the 550–3100 cm^{-1} spectral range. The data from 0 to 550 cm^{-1} has been simulated from DFT calculations.

Table 1
Comparison of the integrated band strengths ($\times 10^{-17}$ cm/molecule) of HFC-43-10mee.

	Spectral bands (cm^{-1})							
	0–550	550–720	720–755	755–910	910–965	965–1600	2850–3100	Total[a]
Experimental data								
This study (305 K)		1.70	0.32	0.77	0.07	27.24	0.20	30.97 ± 1.09
This study (320 K)		1.65	0.31	0.75	0.07	26.53	0.21	30.18 ± 1.68
This study (340 K)		1.72	0.33	0.81	0.08	27.44	0.18	31.23 ± 0.93
PNNL [7] (278 K)		1.73	0.31	0.73	0.05	27.17	0.10	30.77 ± 0.92
PNNL [7] (298 K)		1.69	0.31	0.73	0.05	27.07	0.10	30.63 ± 0.92
PNNL [7] (323 K)		1.74	0.32	0.75	0.05	28.04	0.10	31.68 ± 0.95
Theoretical data								
DFT pure *threo*	1.14	1.52	0.27	0.41	0.00	30.34	0.10	33.78
DFT pure *erythro*	0.60	1.98	0.36	0.96	0.059	30.10	0.10	34.16
DFT mixture	0.68	1.92	0.35	0.88	0.05	30.13	0.10	34.11

[a] For the sake of comparison, the total values for the experimental data include the 0–550 cm^{-1} band from the DFT mixture
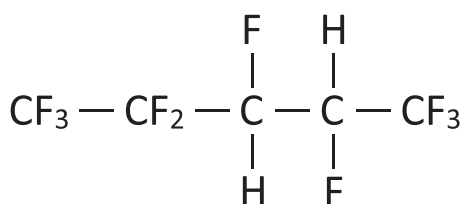
(a) *Threo*-HFC-43-10mee
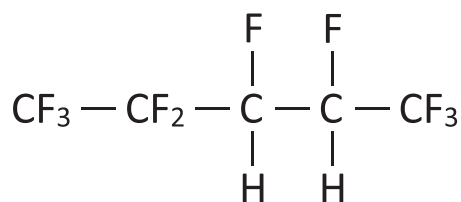
(b) *Erythro*-HFC-43-10mee

Fig. 2. Structure of the two diastereoisomers of HFC-43-10mee.

mated by the authors to be around 3%. Due to the large natural widths of the bands, the pure vapour spectra of this study overlap very well with the PNNL broadened spectra, the only exception being in the spectral ranges where unresolved rovibrational transitions are visible in the pure vapour spectra. The total integrated band strength from this study is consistent with the data from the PNNL database (see Table 1).

The theoretical and experimental data do not agree so well, with the theoretical total integrated band strength being about 10% higher than its experimental counterparts. However, this discrepancy between the theoretical and experimental band strengths is still on par with the values observed on other halocarbons using similar levels of theory [9,10].

4. Radiative efficiency and global warming potential

The radiative efficiency and global warming potential of HFC-43-10mee was calculated using the methodology suggested by Hodnebrog et al. [11]. An instantaneous RE was determined from the pure vapour absorption cross-section spectrum at 305 K using a lifetime of 16.1 years. This initial value was then increased by 10% to account for the stratospheric temperature adjustment. Due to the intermediate lifetime of the compound, it was assumed that the main loss was due to reactions with OH in the troposphere. The non-uniform distribution of HFC43-10-mee has thus been accounted for by applying a lifetime correction to the RE using the *S*-shaped fit of Hodnebrog et al. [11].

As seen in Table 2, the lifetime-corrected RE of 0.359 W m^{-2}-ppb^{-1} resulting from this present work experimental cross-section spectrum at 305 K agrees very well with the lifetime-corrected RE calculated from the PNNL spectrum at 298 K. The new HFC-43-10mee GWP$_{100}$ of 1410 leads to a decrease of 14.5% relative to the current AR5 value of 1649.

As mentioned previously, the results from Chen et al. [8] and Arnold et al. [3] strongly suggest that the isomeric composition of HFC-43-10mee does not vary significantly over the lifetime of the compound. Nevertheless, the theoretical radiative efficiency and global warming potential associated with each diastereomer were calculated independently. Although the theoretical REs and GWPs are overestimated relative to their experimental counterparts, the closeness of the values between the diastereomers suggests that even a small variation of the atmospheric *erythro/threo* ratio should not significantly modify the impact of the compound on the atmosphere.

5. Conclusions

Experimental composite absorption cross-section spectra of a pure vapour of HFC-43-10mee from 550 to 3500 cm^{-1} were presented. The comparison between theoretical and experimental results showed that the dominant diastereomer is *erythro*-HFC-

Table 2
Instantaneous and lifetime-corrected radiative efficiencies of HFC-43-10mee in W m^{-2} ppb^{-1} and their corresponding global warming potentials over 20 and 100 years calculated from 0 to 3000 cm^{-1}.

	Instant. RE	Lifetime corr. RE	GWP$_{20}$	GWP$_{100}$
This work (305 K)	0.338	0.359	1005	1410
PNNL [7] (298 K)	0.332	0.353	987	1385
AR5		0.42	1175	1649
DFT *threo*	0.444	0.473	1321	1854
DFT *erythro*	0.434	0.462	1290	1810
DFT mixture	0.435	0.463	1295	1817

43-10mee. The new experimental data agree very well with the broadened HFC-43-10mee spectra from the PNNL database. However, the theoretical calculations by DFT using the B3LYP/6-311 +G(2d,p) basis set overestimate the total integrated band strength by about 10%. Adding a simulated theoretical absorption spectrum in the 0–550 cm^{-1} spectral range to our experimental data, we found a new lifetime-corrected RE of 0.359 $W\,m^{-2}\,ppb^{-1}$ and a GWP_{100} of 1410.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2017.06.004.

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